Articles

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Numerical Analysis of Aqueous Polysulfide Solutions and Its Application to Cadmium Chalcogenide/Polysulfide Photoelectrochemical Solar Cells

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The computer iterative technique is applied to the calculation of the various species in aqueous alkali-metal polysulfide solutions, including OH^-, H^+, H_2S, HS^-, S^{2-}, S_2^{2-}, S_3^{2-}, S_4^{2-}, S_5^{2-}, water, and alkali-metal cations. The distribution of these 11 species is calculated from mass and equilibria constraints in the system upon input of the sulfur, alkali-metal sulfide, and alkali-metal hydroxide concentrations in solution. Reanalysis and regeneration of known polysulfide spectra provide new spectral constants and new equilibria constants that vary by up to 1 order of magnitude from previous values. From the calculated distribution of species in various polysulfide electrolytes, the rate of disproportionation of these electrolytes is calculated, and it is shown that the electrolyte instability can explain the gradual degradation of polysulfide-based photoelectrochemical cells.

Substantial interest has arisen in aqueous polysulfide solutions as primary electrolytes in photoelectrochemical solar cells (PEC).[1] The aqueous alkali-metal polysulfide system is known to contain, in addition to H_2O and alkali-metal cations, OH^-, H^+, H_2S, HS^-, S^{2-}, S_2^{2-}, S_3^{2-}, S_4^{2-}, and S_5^{2-}. Giggenbach has provided evidence that protonated polysulfide species (HS_x^-, x = 2–5) do not occur in significant concentrations in alkaline polysulfide solutions and suggested that the species in solution may be related by the equilibria[2]

$$H_2S \rightleftharpoons H^+ + HS^- \tag{1}$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \tag{2}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{3}$$

$$(x-1)S_{x+1}^{2-} + HS^- + OH^- \rightleftharpoons xS_x^{2-} + H_2O \qquad x = 2\text{–}4 \tag{4}$$

which provides the equilibria equations

$$K_1 = a_{H^+}a_{HS^-}/a_{H_2S} = a_{H^+}f_{HS^-}[HS^-]/f_{H_2S}[H_2S] \tag{5}$$

$$K_2 = a_{H^+}a_{S^{2-}}/a_{HS^-} = a_{H^+}f_{S^{2-}}[S^{2-}]/f_{HS^-}[HS^-] \tag{6}$$

$$K_w = a_{H^+}a_{OH^-}/a_w = a_{H^+}f_{OH^-}[OH^-]/a_w \tag{7}$$

$$K_A = a_{S_2^{2-}}{}^2a_w/a_{HS^-}a_{OH^-}a_{S_3^{2-}} = (f_{S_2^{2-}}[S_2^{2-}])^2/f_{S_3^{2-}}[S_3^{2-}]f_{HS^-}P \tag{8}$$

$$K_B = a_{S_3^{2-}}{}^3a_w/a_{HS^-}a_{OH^-}a_{S_4^{2-}}{}^2 = (f_{S_3^{2-}}[S_3^{2-})]^3/(f_{S_4^{2-}}[S_4^{2-}])^2f_{HS^-}P \tag{9}$$

$$K_C = a_{S_4^{2-}}{}^4a_w/a_{HS^-}a_{OH^-}a_{S_5^{2-}}{}^3 = (f_{S_4^{2-}}[S_4^{2-}])^4/(f_{S_5^{2-}}[S_5^{2-}])^3f_{HS^-}P \tag{10}$$

where

$$P = [HS^-]f_{OH^-}[OH^-]/a_w \tag{11}$$

and a_i, f_i, and [i] are the respective activity, activity coefficient, and concentration of the i species in solution. The water equilibrium constant, K_w, and first acid dissociation constant of H_2S, K_1, are both well-known.[3,4] It has been shown that the second acid dissociation constant of H_2S, K_2, is less than 10^{-17}, significantly smaller than is generally assumed.[5-7] The polysulfide equilibrium constants, K_A, K_B, and K_C, have been studied by Teder,[8] Giggenbach,[2,9] and others.[10,11] To date the most valid studies of the equilibrium constants, employing a more accurate value for K_2, appear to be those of Giggenbach, which were determined by labeling and observed variation of the near-ultraviolet polysulfide absorption spectra.[2,9] However, the accuracy of that study was limited by (i) the strong HS^- absorption spectra, overlapping much of the observed polysulfide spectra, and (ii) the overall complexity of the system, making accurate analysis of these constants extremely difficult.

In this study will be presented a method of numerical analysis to describe the 11 species in aqueous polysulfide solution upon simple input of the temperature and initial concentration of sulfur, alkali-metal hydroxide, and alkali-metal hydrosulfide in solution. The polysulfide equilibria constants will be reevaluated, by compensation of the polysulfide absorption spectrum for the effects of HS^- absorption and by computer analysis of the resultant spectra. This more accurate spectral analysis will yield polysulfide absorption equilibria constants that differ by up to 1 order of magnitude when compared to the constants determined without base-line-corrected spectrophotometry or iterative analyses. We will also demonstrate how polysulfide solution instability, the rate of which is calculated from a knowledge of the species present in the solution, can explain the long-term degradation of polysulfide-based PEC's.

Experimental Section

Electrolyte Preparation. Aqueous sulfide and polysulfide solutions were prepared with commercially available sodium or potassium hydroxide, sodium sulfide, and sulfur. The other alkali-metal hydrosulfides or sulfides are not available and were prepared according to ref 12 by saturation of aqueous alkali-metal hydroxide solution with H_2S:

$$MOH + H_2S \rightarrow MHS + H_2O \tag{12}$$

Alkali-metal sulfide is then nominally formed upon addition of hydroxide:

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$$\mathrm{MOH} + \mathrm{MHS} \rightarrow \mathrm{M_2S} + \mathrm{H_2O} \qquad (13)$$

Absorption Spectra. Spectroscopic measurements were made at 20 °C in a UVIKON 810 spectrometer using a quartz cell of path length 0.2 cm.

Results and Discussion

Calculation of the Species in Polysulfide Solution. An aqueous solution containing only alkali-metal hydroxide, alkali-metal hydrosulfide, and sulfur is restricted by several mass constraints. The cation concentration in solution is given by

$$[\mathrm{M^+}] = [\mathrm{MOH}]_{\mathrm{initial}} + [\mathrm{MHS}]_{\mathrm{initial}} \qquad (14)$$

The total sulfide in solution is restricted by that originally added:

$$[\mathrm{MHS}]_{\mathrm{initial}} = [\mathrm{H_2S}] + [\mathrm{HS^-}] + \sum_{i=1}^{5}[\mathrm{S}_i^{2-}] \qquad (15)$$

Added sulfur is distributed among the polysulfide species in solution:

$$[\mathrm{S}]_{\mathrm{initial}} = \sum_{i=2}^{5}(i-1)[\mathrm{S}_i^{2}] \qquad (16)$$

The hydroxide in solution results from (i) that originally added to solution, (ii) that produced in the protonation of hydrosulfide (eq 12), (iii) that produced in the self-disproportionation of water (eq 3), and (iv) that consumed in the production of divalent sulfide and polysulfide species (eq 4 and 13):

$$[\mathrm{OH^-}] = [\mathrm{MOH}]_{\mathrm{initial}} + [\mathrm{H_2S}] + [\mathrm{H^+}] - \sum_{i=1}^{5}[\mathrm{S}_i^{2-}] \qquad (17)$$

Note that if alkali-metal sulfide (in addition to, or instead of, alkali-metal hydrosulfide) is added to solution, this may be alternatively written as equal concentrations of alkali-metal hydroxide plus alkali-metal hydrosulfide (eq 13) and the mass constraining equations 14–17 remain applicable.

Significant concentrations of S_2^{2-} and S_3^{2-} exist only in very alkaline polysulfide solutions. Hence, two of the equilibrium constants, K_A and K_B, are only measurable in extremely alkaline conditions, necessitating high ionic strength and preventing reasonable extrapolation to dilute solutions.

In his spectral measurements on polysulfide solutions, Giggenbach[9] uses a term to describe the polysulfide environment, analogous to eq 11, and assumes unit activity coefficients for all species in solution, with the exception of $a_{\mathrm{H^+}}$, which is estimated as the colorimetrically measured hydrogen ion activity.[13] Serious deficiencies in colorimetric determination of pH in alkaline solution have recently been discussed.[14]

Improvement can be made over previous calculations by direct measurement of the pH, even in concentrated alkaline solution.[14] Mean solution activity coefficients are not known for polysulfide solutions, and we therefore make the following estimations:

The hydroxide activity coefficient and water activity are equivalent to the known mean solution activity coefficients for an alkali-metal hydroxide solution of the same cationic strength

$$f_{\mathrm{OH}} = f_{\pm_{\mathrm{MOH}}}([\mathrm{M^+}]) \qquad (18)$$

$$a_{\mathrm{w}} = a_{\mathrm{w_{MOH}}}([\mathrm{M^+}]) \qquad (19)$$

and relative trends of the various (poly)sulfide activity coefficients tend to cancel. For example in eq 8–10

$$(f_{\mathrm{S}_{x+1}^{2-}})^{x+1}/(f_{\mathrm{S}_x^{2-}})^{x}f_{\mathrm{HS^-}} = 1 \qquad x = 2\text{–}4 \qquad (20)$$

The assumptions inherent in eq 18–20 are an improvement compared to the calculation of purely concentration-dependent equilibrium constants. As improved approximations, the assumptins made in eq 18 and 19 are reasonable; in dilute solutions the Debye–Hückel theory yields similar alkali-metal cation and hydroxide activity coefficients,[15] and in concentrated solutions hydration of the cation, by binding of free solvent, tends to dominate water and ion activity coefficient variation. Similarly, although the absolute magnitude of sulfide or polysulfide activity coefficients will vary as a function of concentration, electrostatic and hydration effects will tend to cancel, and relative variations, as expressed by eq 20, will be smaller. However, if polysulfide mean activity coefficients become available, calculations can be further improved by their inclusion.

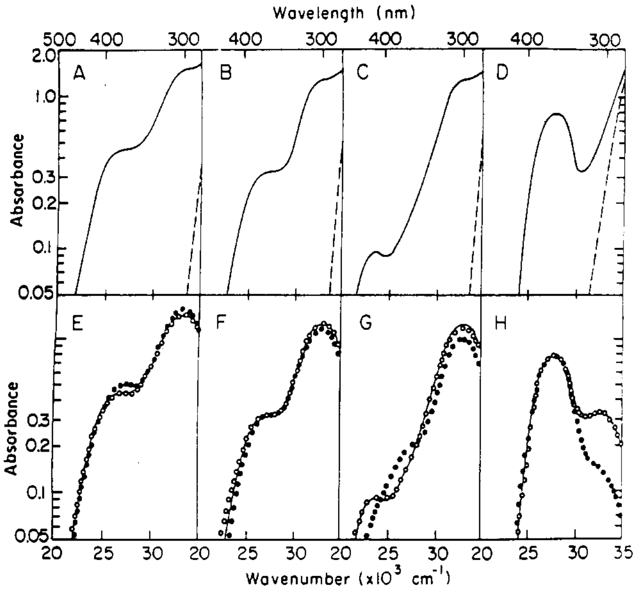

Figure 1. Known spectra[9] of polysulfide solutions (solid lines) containing 0.2 M Na_2S and 0.005 M S, compared to measured spectra of solutions that were similar but contained no added sulfur (dashed lines) (20 °C, 0.2 cm path length cell): (A) at an ionic strength of 2 M, pH 6.4 (P = –8.3); (B) at an ionic strength of 2 M, pH 10.5 (P = –3.5); (C) in 4.5 M NaOH (P = 0.0); (D) in 18 M NaOH (P = 2.5). The solid lines in spectra E–H are as in spectra A–D, after base-line correction for HS^- and S^{2-} absorption, with computer-generated spectra using spectral and dissociation constants according to Giggenbach (closed circles) and this work (open circles) being presented also.

Given known initial concentrations of alkali-metal hydroxide, alkali-hydrosulfide, and sulfur, the computer iterative technique is then applied to calculate the distribution of species in solution. This is accomplished by initially assuming the solution contains only hydroxide, hydrosulfide, and tetrasulfide

$$[\mathrm{OH^-}] \doteq [\mathrm{MOH}]_{\mathrm{initial}} \qquad (21)$$

$$[\mathrm{HS^-}] \doteq [\mathrm{MHS}]_{\mathrm{initial}} \qquad (22)$$

$$[\mathrm{S_4^{2-}}] \doteq [\mathrm{S}]_{\mathrm{initial}}/3 \qquad (23)$$

followed by estimation of all other species through rearrangement and application of eq 5–10 and 18–20:

$$a_{\mathrm{H^+}} = K_{\mathrm{w}}a_{\mathrm{w}}/[\mathrm{OH^-}]f_{\pm_{\mathrm{MOH}}}([\mathrm{M^+}]) \qquad (24)$$

$$[\mathrm{H_2S}] = a_{\mathrm{H^+}}[\mathrm{HS^-}]/K_1 \qquad (25)$$

$$[\mathrm{S^{2-}}] = K_2[\mathrm{HS^-}]/a_{\mathrm{H^+}} \qquad (26)$$

$$[\mathrm{S_5^{2-}}] = ([\mathrm{S_4^{2-}}]^4 a_{\mathrm{H^+}}/K_{\mathrm{C}}K_{\mathrm{w}}[\mathrm{HS^-}])^{1/3} \qquad (27)$$

$$[\mathrm{S_3^{2-}}] = (K_{\mathrm{B}}K_{\mathrm{w}}[\mathrm{HS^-}][\mathrm{S_4^{2-}}]^2/a_{\mathrm{H^+}})^{1/3} \qquad (28)$$

$$[\mathrm{S_2^{2-}}] = (K_{\mathrm{A}}K_{\mathrm{w}}[\mathrm{HS^-}][\mathrm{S_3^{2-}}]/a_{\mathrm{H^+}})^{1/3} \qquad (29)$$

Improved estimations of the hydroxide, hydrosulfide, and tetrasulfide concentrations are then made by normalization of all species to satisfy the mass constraints of eq 14–17. Equations 24–29 are then repeated with use of the improved calculated hydroxide, hydrosulfide, and tetrasulfide concentrations. An error analysis is performed by comparing the input concentrations and

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Table I. Spectral Constants for Aqueous Polysulfide Species[a]

species	peak location p, cm^{-1}	peak width w, cm^{-1}	peak height (mol abs) h
S_2^{2-}	27 900	2200	990
S_3^{2-}	23 300	3300	206
	33 100	3300	2600
S_4^{2-}	26 900	2900	1140
	33 100	2900	3690
S_5^{2-}	26 500	3600	1800
	33 800	3600	6800

[a] Spectral constants are determined from a fit of Figure 1E–H. Total absorbance, in a cell of path length d, at frequency v, with HS^- and S^{2-} absorbance excluded, is given by $A(v) = d\sum_{i=1}^{5}[S_i^{2-}]h_ie^{-[(b-p_i)/w_i]^2}$.

Table II. Equilibrium Constants for the Aqueous Polysulfide System[a]

K	a	b	c	ref
K_1	−2830.4	0.02083	8.7289	*b*
K_2	−28646.0	−0.26570	158.255	*c*
K_w	−3927.1	0.01223	2.8334	3
K_A	0	0	−4.18 (±0.3)	*d*
K_B	0	0	−0.35 (±0.3)	*d*
K_C	0	0	5.6 (±0.6)	*d*

[a] $\log K = a/T - bT + cT =$ temperature (K). K_A, K_B, and K_C are determined from a fit of Figure 1E–H. [b] By fit of data in ref 4. [c] By fit of data in ref 5. [d] This work.

all equilibria constants to those determined with use of the calculated species distribution in solution. The entire process is repeated until the calculated distribution of species in solution reproduces each of the initial concentration and equilibria conditions to better than 0.01%.

Polysulfide Dissociation Constants. In Figure 1A–D are presented the known absorption spectra of a variety of polysulfide solutions.[9] Sulfide and hydrosulfide species absorb strongly in the near-UV region, and the near-UV side of the spectra in Figure 1A–D are dominated by these absorptions. In the solid curves presented in Figure 1E–H, we have compensated for the strong sulfide and hydrosulfide absorptions by subtracting out our base-line measurements made on solutions that were similar but contained no sulfur. Identification of the various absorption peaks in the spectra was accomplished by Giggenbach.[9] However, determination of the precise peak locations and widths were complicated by the strong overlap between the various absorptions. This has been resolved by computer analysis and regeneration of the spectra in which compensation, by base-line subtraction of overlapping peaks, allows precise measurement of these constants. These revised polysulfide spectral peak locations and widths are presented in Table I and differ by up to 700 cm^{-1} when compared to the values calculated without base-line correction by Giggenbach. As seen in the solid curve in Figure 1H, in polysulfide solutions containing 0.2 M Na_2S and 0.005 M sulfur and having hydroxide concentration such that $P = 2.5$, an absorption appears at 27 900 cm^{-1}, attributable[9] to S_2^{2-}. This peak diminishes with pH, until at $P = 0.0$, as seen in Figure 1G, it is replaced by absorptions at 23 300 and 33 100 cm^{-1} attributable to S_3^{2-}. Further diminishing of pH, to $P = -3.5$, seen in Figure 1F, reveals a new peak at 26 900 cm^{-1}, attributable to S_4^{2-}. Finally, as seen in Figure 1E, additional peaks, attributable to S_5^{2-}, are evident at 26 900 and 33 800 cm^{-1}, upon final lowering of the pH to 6.4 and $P = 8.3$.

The distribution of species in polysulfide solutions containing 0.2 M Na_2S and 0.005 M sulfur at various pH values was calculated according to the procedure described in the previous part, with use of known values of K_w, K_1, and K_2, as presented in Table II, and various values of K_A, K_B, and K_C. Computer-simulated polysulfide spectra were then generated from the spectral constants and the calculated distribution of polysulfide species. Compared in Figure 1E–H are computer-generated spectra we have constructed using (i) the polysulfide equilibria constants, K_A, K_B, and K_C, and the spectral constants presented by Giggenbach[9] (closed circles) and (ii) those constants determined to provide a best fit to the spectra (open circles). The best fit of the spectra is accomplished by using the absorption peak locations and widths provided in Table I and varying the peak heights (absorptivities) and the values of K_A, K_B, and K_C until an optimum fit of the spectra is achieved. Absorptivities determined to provide the best fit are presented in Table I and best polysulfide equilibrium constants in Table II. These differ by up to 1 order of magnitude compared to the equilibrium constants determined by Giggenbach,[2,9] and it is seen, in Figure 1, that our determined constants results in a substantially better representation of the observed spectra. Giggenbach observed no variation of the polysulfide dissociation constants with temperature,[2] and we assume this to be the case here. Note that no attempt is made at equilibrium constant correction for variation in ionic strength. As discussed, two of the constants, K_A and K_B, are only measurable in solutions of high ionic strength and cannot be extrapolated to dilute solutions.

Error Analysis. As discussed in the previous part, calculations are converged to within 0.01%. There is a degree of flexibility in fitting the observed spectra by varying the magnitude of the polysulfide absorptivities to partially compensate for variations

Table III. Calculated Distribution of Species within a Polysulfide Solution Containing 2.5 *m* Sulfur and Different Concentrations of Potassium Hydroxide and Sulfide[a]

	temp, °C; concn, mol/kg of H_2O[b]					
	20; 2, 1.4	60; 2, 1.4	20; 0, 1.4	60; 0, 1.4	20;[2] 0, 2.6	60; 0, 2.6
			Assumed Activity Coefficients			
F	1.66	1.36	1.03	0.92	1.84	1.49
a_w	0.771	0.747	0882	0.887	0.700	0.761
			Calculated Activities			
OH^-	3.90	3.22	0.44	0.40	2.75	2.24
H^+	1.40×10^{-15}	2.28×10^{-14}	1.43×10^{-14}	2.10×10^{-13}	1.93×10^{-15}	3.18×10^{-14}
K^+	7.95	6.55	2.87	2.56	9.56	7.73
H_2O	42.8	43.5	48.9	49.2	4.4	42.3
			Calculated Concentrations			
H_2S	5.32×10^{-9}	4.16×10^{-8}	6.60×10^{-8}	4.61×10^{-7}	3.11×10^{8}	2.44×10^{7}
HS^-	0.351	0.359	0.43	0.43	1.50	1.51
S^{2-}	0.001 11	0.000 887	0.000 134	0.000 116	0.003 44	0.002 67
S_2^{2-}	0.006 95	0.006 26	0.002 01	0.001 88	0.0135	0.0120
S_3^{2-}	0.535	0.515	0.323	0.314	0.675	0.649
S_4^{2-}	0.501	0.514	0.633	0.638	0.409	0.426
S_5^{2-}	0.004 87	0.005 34	0.0129	0.0135	0.002 57	0.002 90

[a] Calculated by using equilibrium constants in Table II according to the method described in the text. The activity coefficient of all species in solution is considered unity except for F, the activity coefficient for OH^- and K^+, and a_w, the activity coefficient of water. F and a_w are values for potassium hydroxide solutions of the same cationic strength. [b] Concentrations are those of KOH and K_2S, respectively.

Table IV. Calculated Time (Days) for Half the Free Sulfur To Disproportionate to Thiosulfate and Hydrosulfide in Polysulfide Solutions Containing 2.6 *m* Sulfur and Different Concentrations of Potassium Hydroxide and Sulfide[a]

	concn, mol/kg of H_2O[b]		
	2, 1.4	0, 1.4	0, 2.6
t_h(20 °C)	5400	27000	260000
t_h(60 °C)	31	148	1480

[a] The half-life, t_h, is calculated from eq 30 with use of data from Table III. [b] Concentrations are those of KOH and K_2S, respectively.

in equilibrium constants. However, beyond even a factor of 2 variation from the best fit equilibria values, subsequent variation of the absorptivities is not adequate to compensate for deviations in the curves and results in visibly poorer fits compared to the observed spectra. The large error we attach to the polysulfide equilibrium constants, in Table II, represents the flexibility available in fitting the spectra.

As an example of the use to which this analysis can be applied, we derive the thermodynamic (in)stability of some aqueous polysulfide solutions.

Thermodynamically, aqueous polysulfide solutions are unstable. Giggenbach observed that polysulfide spontaneously disproportionates in solution according to the reaction[16]

$$S_5^{2-} + 3OH^- \rightarrow S_2O_3^{2-} + 3HS^- \qquad (30)$$

In CdX/S_x PEC's, the resultant thiosulfate may then undergo photoinduced oxidation.[17] The half-life of a polysulfide solution may be defined as the time for half of the free sulfur (as polysulfide) to disproportionate. This time, t_h, is given by[16]

$$t_h \text{ (days)} = 10^{5600/T-16.6}[S]_{\text{initial}}[HS^-]^2/a_{OH^-}[S_5^{2-}] \qquad (31)$$

where T is the temperature in degrees Kelvin. The distribution of species, calculated by the aforementioned numerical methods for a solution of 2 *m* KOH, 1.4 *m* K_2S, and 2.6 *m* S is presented in Table III. The calculated useful half-lives of polysulfide solutions, calculated by eq 31 and using data from Table III are presented in Table IV. In these solutions, Table IV indicates that, at 60 °C, 50% of the dissolved sulfur is expected to disproportionate after approximately 1 month.

Analysis (by precipitation with $BaCl_2$) of the electrolyte in two Cd(Se·Te)/S_x^{2-} PEC's, removed from cells that had operated outdoors for several years, showed that approximately 70% of the polysulfide in solution had decomposed to sulfate or thiosulfate. This shows that the solution itself is unstable with time. It has been shown that the photoelectrode is considerably less stable in weaker polysulfide electrolytes.[19] We have found that such PEC's are considerably less stable in summer than in winter (illumination intensity, which could also be a cause of this, varies much less with the seasons than does the temperature) and also that insulated cells, which reach temperatures ca. 10 °C higher than noninsulated cells, are much less stable, which follows from the calculations shown in Table IV. We thus have the result that a primary effect, solution instability, leads to weaker polysulfide electrolytes, which results in the secondary effect, photocorrosion. As can be seen in Table IV, a small modification in the solution can increase polysulfide lifetimes by several orders of magnitude, which will increase useful electrolyte lifetimes from a month to several years. This has recently led to the experimental verification of extended lifetime photoelectrochemical solar cells.[20]

Conclusions

A numerical technique has been provided for the calculation of the 11 known species in aqueous alkali-metal polysulfide solutions. Computer regeneration of known spectra provide new spectral and equilibrium constants for this system. In view of the significantly different values for K_A and K_B compared to earlier values, thermodynamic parameters constraining the aqueous polysulfide systems, including redox potentials,[21] must be reevaluated.[22] Results from these calculations are used to demonstrate that gradual degradation of polysulfide-based PEC's results primarily from electrolyte instability.

Registry No. H_2S, 7783-06-4; HS^-, 15035-72-0; S^{2-}, 18496-25-8; S_2^{2-}, 16734-12-6; S_3^{2-}, 12597-05-6; S_4^{2-}, 12597-07-8; S_5^{2-}, 12597-12-5.

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